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Hydrogen production by biogas steam reforming: A technical, economic and ecological analysis

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ABSTRACT

Fuel cells are electrochemical energy conversion devices that convert fuel and oxidant electrochemically into electrical energy, water and heat. Compared to traditional electricity generation technologies that use combustion processes to convert fuel into heat, and then into mechanical energy, fuel cells convert the hydrogen and oxygen chemical energy into electrical energy, without intermediate conversion processes, and with higher efficiency. In order to make the fuel cells an achievable and useful technology, it is firstly necessary to develop an economic and efficient way for hydrogen production. Molecular hydrogen is always found combined with other chemical compounds in nature, so it must be isolated. In this paper, the technical, economical and ecological aspects of hydrogen production by biogas steam reforming are presented. The economic feasibility calculation was performed to evaluate how interesting the process is by analyzing the investment, operation and maintenance costs of the biogas steam reformer and the hydrogen production cost achieved the value of 0.27 US$/kWh with a payback period of 8 years. An ecological efficiency of 94.95%, which is a good ecological value, was obtained. The results obtained by these analyses showed that this type of hydrogen production is an environmentally attractive route.

Contents

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Nomenclature

C_{BIOGAS}	Biogas cost (US$/kWh)
C_{FUEL}	Fuel cost (US$/kWh)
C_{OP}	Operational cost (US$/kWh)
C_{MAN}	Maintenance cost (US$/kWh)
CH_4	Methane “(-)”
CO	Carbon Oxide “(-)”
CO_2	Carbon dioxide “(-)”
$(CO_2)_e$	Equivalent carbon dioxide ($kg_{emissions}/kg_{fuel}$)
Cp	Specific heat at constant pressure (kJ/kg.K)
dH	Heat of formation (kJ/kmol)
E	Euler number “(-)”
E_{H2}	Power supplied by hydrogen (kW)
E_{fuel}	Power supplied by fuel (kW)
E_{biogas}	Power supplied by biogas (kW)
E_{STEAM}	Power supplied by steam (kW)
f	Annuity factor (1/year).
H	Equivalent period of operation (h/year)
h	Specific enthalpy (kJ/kmol)
H_2	Hydrogen “(-)”
H_2S	Hydrogen Sulfide “(-)”
H_2O	Water “(-)”
Inv_{REF}	Investment cost in hydrogen production system (US$)
k	Payback period (year)
K	Equilibrium constant “(-)”
Kp	Equilibrium constant in function of partial pressure “(-)”
LHV	Lower heat value (kJ/kg)
m	Mass (kg)
n	Moles number (mol)
Na	Reactant a moles number (mol)
Nb	Reactant b moles number (mol)
Nc	Product c moles number (mol)
Nd	Product d moles number (mol)
NO_x	Nitrogen oxide “(-)”
P	Pressure (atm)
PM	Particulate matter “(-)”
P_0	Pressure at reference state (atm)
Q_i	Fuel low heat value MJ/kg
R	Universal gas constant (kJ/kmol.K)
r	Annual interest rate (%)
SO_2	Sulfur dioxide “(-)”
T	Temperature (°C)
T_0	Temperature at reference state (K)
T_2	Reforming temperature (K)
y_i	Molar fractions of gaseous components “(-)”

Greek letters

α	Advance degree “(-)”
η	Efficiency (%)
ΔG^0	Gibbs energy variation (kJ/kmol)
ΔH^o	Enthalpy change (kJ/kmol)
ΔS^o	Entropy change (kj/kmol.K)
π_g	Pollutant indicator (kg/MJ)
ε	Ecological efficiency (%)

1. Introduction

Successive crises in energy and global warming have been instigating the study for more efficient technologies and renewable sources of electricity generation. In this context, fuel cell has got particular attention. The great interest in hydrogen as an energetic carrier has been increasing, due to its high heating value and the low environmental impact of its use as fuel. The hydrogen can be used to generate electricity by a fuel cell and contributes to increase the distributed generation of energy, and to reduce emissions of pollutants into the environment. This energetic carrier does not directly emit pollutants, but it leads to indirect emissions, since it is found combined with other chemical compounds in nature, thus requiring energy to be isolated and, consequently, releasing pollutants into the environment.

Among several hydrogen production processes, the steam reforming process, using natural gas, is widely used in chemical industries, and it is responsible for 50% of the hydrogen produced in the world [1]. The biogas can be an alternative raw material to conventional steam reforming technology. Biogas is similar to the natural gas, and has included additional benefits such as it is a renewable resource, it reduces emissions by preventing methane release in the atmosphere (methane is 21 times stronger than carbon dioxide as a greenhouse gas), and it is commercially produced in large quantities in anaerobic digesters and landfill gas recovery facilities designed to treat bio-wastes such as manure, sewage, energy crops, and organic matter. The biogas production also reduces landfill waste and produces nutrient-rich fertilizer as by-product [2].

The reform process consists in two reactors (reform reactor and shift reactor). In the reform reactor occur the catalytic reforming reactions of hydrocarbons, like methane, naphtha or ethanol with water (pre-vaporized by a steam generator). The products of these reactions are H_2 (main objective of the reform) and CO. In the shift reactor all CO produced in the reform reactor, react with water steam. The products of this reaction are H_2 and CO_2. So, in the end of the reform process, the main products are hydrogen (H_2) and carbon dioxide (CO_2) [3,4]. Based on this background the feasibility of the hydrogen production by biogas steam reforming process stands out in this paper.

2. Biogas steam reforming technical analyses

In the physicochemical analysis of biogas steam reforming, some calculations involving chemical and thermodynamics functions were performed, which made possible to find the optimum pressure and temperature of the reforming reaction, in order to optimize the construction of the reformer prototype.

The analysis was based on the biogas obtained by the bovine manure biodigester located at the Laboratory of Optimization of Energy Systems (LOSE-UNESP); after the purification process, the composition of biogas was 75.7% of CH_4, 24.3% of CO_2.

The biogas reform, according to the literature [5,6], was considered to be the methane steam reforming and the methane dry reforming (in the reform reactor, before of shift reactor) as the following reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (methane steam reformer)} \quad (1)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \text{ (methane dry reformer)} \quad (2)$$

Considering 100 g of biogas (75.7 g of CH_4 and 24.3 g of CO_2) and that all CO_2 reacts in the dry reform, it was found that 8.83 g of CH_4 react in dry reform. So, considering that the CH_4 total is 75.7 g, the quantity of this component that reacts in the steam reforming is 66.9 g. Thus, the final reaction of biogas is composed of 66.9% of

steam reform and 33.1% of dry reform, as the reaction shown below:

$$0.669 \text{ steam reforming} + 0.331 \text{ dry reforming} = \text{biogas final reforming} \quad (3)$$

In the shift reactor all CO produced by steam reforming and dry reforming react with water steam and the products of these reactions are H_2 and CO_2, as shown in the following equation [7].

$$CO+H_2O \rightarrow CO_2+H_2 \text{ (shift reaction)} \quad (4)$$

2.1. Variation of Gibbs energy

Gibbs energy is a thermodynamic function that predicts whether a process is spontaneous or not. The variation of Gibbs free energy (ΔG^o) depends exclusively on the initial and final states of the system. When the system is in a constant temperature and pressure and the substances involved are in standard condition, we can calculate the Gibbs free energy as shown in the following equation [8,9].

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \quad (5)$$

If there is any phase changed in the range of the temperature (T) studied, the corresponding values of entropy (ΔS) and enthalpy (h) should be taken into account, leading to a generalized form of Gibbs Free Energy as shown in the following equation [10]:

$$\Delta G^o = a + bT.\log\ T + cT2 + eT{-}1 + fT \quad (6)$$

when $\Delta G < 0$ the reaction occurs in a direct and spontaneous way, when $\Delta G > 0$ the reaction does not occur in a spontaneous way and when $\Delta G = 0$ the reaction is in equilibrium [9].

Fig. 1 shows the Gibbs free energy to the reactions that occur in reactor 1 (steam reforming, dry reforming and final reforming) and Fig. 2 shows the Gibbs free energy to the reaction that occurs in reactor 2 (Shift Reactor).

As shown in Fig. 1, at around 650 °C, the Gibbs energy becomes null, indicating that the reaction is only possible at high temperatures, showing that this process is endothermic. In Fig. 2, until around 800 °C, the Gibbs energy is negative, indicating that the reaction is only possible at low temperatures, indicating that this reaction is exothermic.

2.2. Equilibrium constant analysis

The equilibrium constant associated with the reaction of biogas reforming and the formula that determines the mole fractions of reactants and products can be expressed as indicated by the following equations [8]:

$$K = e^{-(\Delta G^0/RT)} \quad (7)$$

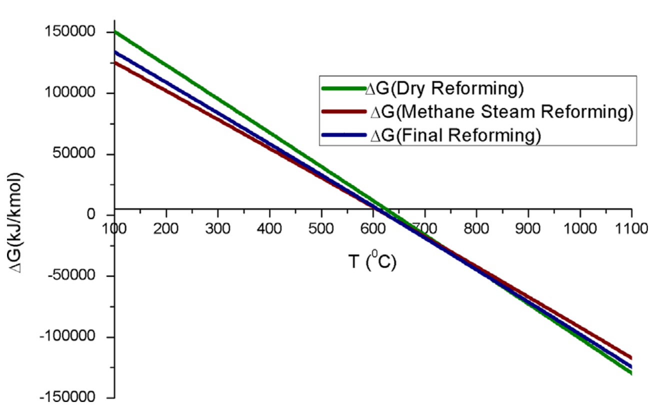

Fig. 1. Gibbs energy of the biogas reform.

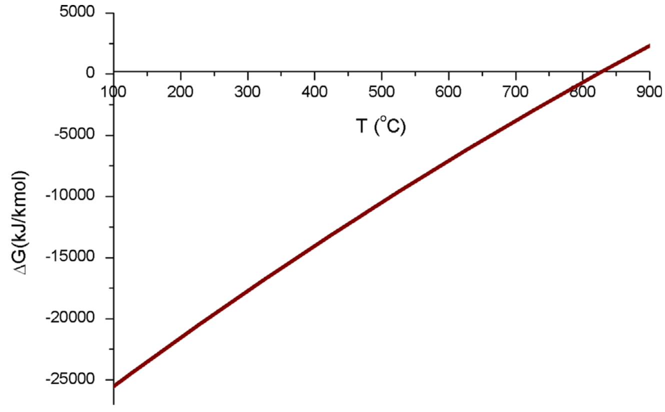

Fig. 2. Gibbs energy of the shift reaction.

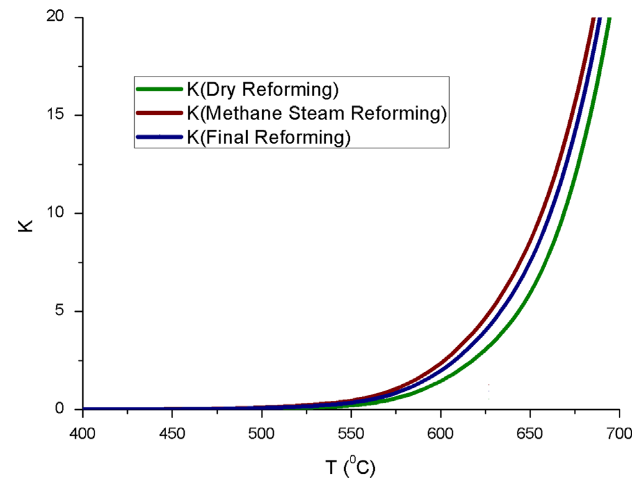

Fig. 3. Equilibrium constant in reactor 1 as a function of temperature.

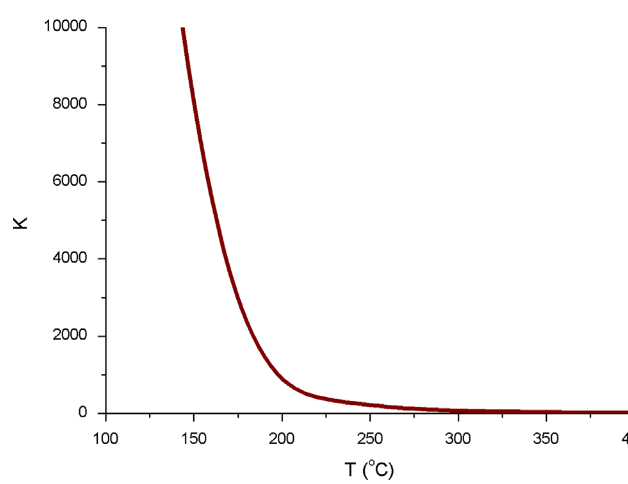

Fig. 4. Equilibrium constant in reactor 2 as a function of temperature.

$$\left[\frac{y^{nc}.y^{nd}}{y^{na}.y^{nb}}.\left(\frac{P}{P_0}\right)^{nc+nd-na-nb}\right] = e^{-(\Delta G^0/RT)} \quad (8)$$

$$y_i = \frac{n_i}{n_{TOT}} \quad (9)$$

It was considered that the equilibrium constant (K) is equal to equilibrium constant in a function of partial pressure (Kp) [9]

Table 1
Chemical equilibrium of methane steam reforming reaction and dry reforming.

	Methane steam reforming				Dry reforming			
(a)								
	$CH_4+H_2O \leftrightarrow CO+3H_2$				$CH_4+CO_2 \leftrightarrow 2CO+2H_2$			
Beginning:	n	n	0	0	n	n	0	0
Number of moles:	$n^0=n+n=2n$				$n^0=n+n=2n$			
	Equilibrium:				Equilibrium:			
Number of moles:	$n(1-\alpha)$	$n(1-\alpha)$	$n\alpha$	$3n\alpha$	$n(1-\alpha)$	$n(1-\alpha)$	$2n\alpha$	$2n\alpha$
(b)								
	Methane steam reforming							
Total number of moles:	$n_{\text{equilibrium}}=n(1-\alpha)+n(1-\alpha)+n\alpha+3n\alpha=2n(1-\alpha)+4n\alpha=2n+2n\alpha$							
	$n_{\text{equilibrium}}=2n\ (1+\alpha)$							
Atomic fraction:	$n(1-\alpha)/2n(1+\alpha)$	$n(1-\alpha)/2n(1+\alpha)$	$n\alpha/2n(1+\alpha)$	$3n\alpha\ /2\ n(1+\alpha)$				
	$(1-\alpha)/2(1+\alpha)$	$(1-\alpha)/2(1+\alpha)$	$\alpha/2(1+\alpha)$	$3\alpha/2(1+\alpha)$				
	Dry reforming							
Total number of moles:	$n_{\text{equilibrium}}=n(1-\alpha)+n(1-\alpha)+2n\alpha+2n\alpha=2n(1-\alpha)+4n\alpha=2n+2n\alpha$							
	$n_{\text{equilibrium}}=2n\ (1+\alpha)$							
Atomic fraction:	$n(1-\alpha)/2n(1+\alpha)$	$n(1-\alpha)/2n(1+\alpha)$	$2n\alpha/2n(1+\alpha)$	$2n\alpha\ /2\ n(1+\alpha)$				
	$(1-\alpha)/2(1+\alpha)$	$(1-\alpha)/2(1+\alpha)$	$\alpha/(1+\alpha)$	$\alpha/(1+\alpha)$				

Table 2
Chemical equilibrium of shift reaction.

	$CO+H_2O \leftrightarrow CO_2+H_2$			
(a)				
Beginning:	n	n	0	0
Number of moles:	$n^0=n+n=2n$			
Equilibrium:				
Number of moles:	$n(1-\alpha)$	$n(1-\alpha)$	$n\alpha$	$n\alpha$
(b)				
Total number of moles:	$n_{\text{equilibrium}}=n(1-\alpha)+n(1-\alpha)+n\alpha+n\alpha=2n(1-\alpha)+2n\alpha=2n$			
	$n_{\text{equilibrium}}=2n$			
Atomic fraction:	$n(1-\alpha)/2n$	$n(1-\alpha)/2n$	$2n\alpha/2n$	$2n\alpha/2\ n$
	$(1-\alpha)/2$	$(1-\alpha)/2$	$\alpha/2$	$\alpha/2$

Table 3
Equilibrium constant.

Methane steam reaction	$k=\frac{2^6\alpha^5P^2}{(3+2\alpha)^2(1-\alpha)^3}$
Dry reaction	$k=\frac{4\alpha^4}{(1+\alpha)^2(1-\alpha)^2}$
Final biogas reforming	$K=0.669K_{\text{reforma a vapor}}+0.331K_{\text{reforma a seco}}$
Shift reaction	$K=\frac{\alpha^2}{(1-\alpha)^2}$

The equilibrium constant values as temperature function to Reactors 1 and 2 are shown in Figs. 3 and 4, respectively.

2.3. Advance degree

The Advance Degree (α) indicates the progress level of each reaction according to the temperature and pressure of the reaction, and it ranges between 0 (chemical reactions do not occur) and 1 (when all reactants are converted into products) [11].

A physicochemical analysis was performed in order to make this analysis more accurate. The equilibrium compositions of biogas steam reforming and dry reforming according to the temperature can be determined by setting the equilibrium of chemical reactions as shown in Table 1(a) and (b), respectively. Table 2(a) and (b) show the equilibrium compositions of shift reaction.

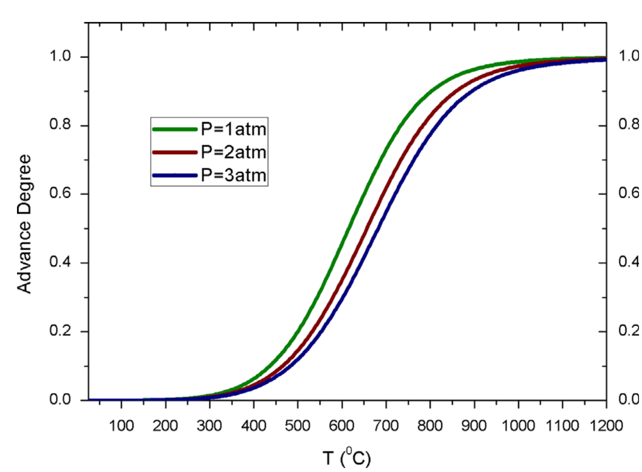

Fig. 5. Behavior of the advance degree in different operating ranges (biogas final reforming reaction).

Table 3 shows the equilibrium constants of the reactions.

According to Castellan [12], the value of α increases as the reaction occurs, reaching the limit value when one or more reactants are consumed. Thus, the limit value of the advance degree means the capacity in which the reaction happens.

The behavior analysis of the advance degree in different ranges of temperatures and pressures of the studied reactions (final biogas reforming and shift reaction) can be observed in Figs. 5 and 6 respectively.

It can be noticed in Fig. 5 that, the advance degree of biogas reforming considerably varies, regardless of pressure, at operating temperatures above 500 °C. It can also be noticed that the advance degree tends to become constant in operating temperatures above 700 °C, regardless of the pressure too. The best pressure for the conversion in all cases is 1 atm and the best temperatures are between 700 °C and 900 °C. In the case of shift reaction, it can be noticed in Fig. 6 that the conversion rate of reactants to products is not favored by high temperature; the pressure does not affect this process. At temperatures higher than 200 °C, the advanced degree starts to decrease.

The temperature of natural gas steam reforming reported in the literature [13,14] was in the range of 800–1000 °C, next to the values calculated for the biogas. This is due to the fact that both fuels have the methane as its main component the methane. The same occurs in the shift reaction, in the literature the temperature found of the reaction ranges in 140–350 °C, value next to calculated by physicochemical analysis [15,16].

3. Efficiency of biogas steam reforming

The theoretical efficiency of steam reforming process was calculated, considering that the reform is not a continuous process. Therefore, a biogas storage tank between the biogas production sector and the reformer was considered. In this way, it is possible to assume the required biogas stream.

In the calculation of the process efficiency, it was considered that the reactions occurs in both the reactors (reform reactor and shift reactor), since the process efficiency is according to the amount of hydrogen produced (Table 4). It also considered that the reform is composed of boiler and reactors, and the fuel used to produce steam was biogas, as shown in Fig. 7.

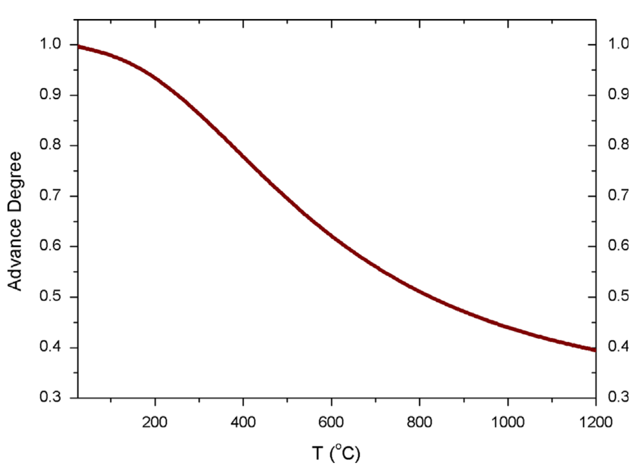

Fig. 6. Behavior of the advance degree in different operating ranges (shift reaction).

To calculate the efficiency of the biogas reform process a mass balance was performed, as shown in Eq. (10).

The total hydrogen produced was considered, according to the final reaction of the biogas (steam reforming+dry reform+shift). The biogas used in the reformer was calculated by considering the methane necessary to produce the amount of hydrogen, according to the final reaction of the biogas, plus the carbon dioxide of its composition. The biogas used in the boiler was calculated by the amount of steam necessary for the reform process, considering the boiler efficiency as 80% [17]:

$$\eta_{\text{Rbiogas}} = \frac{m_{H_2} LHV_{H_2}}{(m_{\text{biogas reform}} LHV_{\text{biogas reform}}) + (m_{\text{biogas boiler}} LHV_{\text{biogas boiler}})} \tag{10}$$

where

LHV $_{H2}$: 119,742.48 kJ/kg [18]
LHV $_{CH4}$: 49,934.28 kJ/kg [19]

The LHV of biogas is calculated by the following equation [19]:

$$LHV_{\text{biogas}} = LHV_{\text{methane}} \% CH_4 = 37,850.2 \text{ kJ/kg} \tag{11}$$

The efficiency of the reformer process was 80%. Comparing the efficiency of the biogas steam reforming with the traditional process (using natural gas), it can be noticed that the efficiency is almost the same. According to the literature [14] the efficiency of natural gas reforming is 85%. The little difference in the efficiency of both the processes can be justified by the fact that the amount of methane in natural gas is higher than in the biogas, and the methane is mainly responsible for hydrogen production in the case of steam reforming of both the substances.

4. Economic analysis

The economic analysis was based on the methodology developed by Silveira et. al. [20]. It allows the evaluation of the attractiveness of the biogas steam reforming process by analyzing the investment, operation and maintenance costs, as well as the expected annual revenues to the commercialization of obtained products.

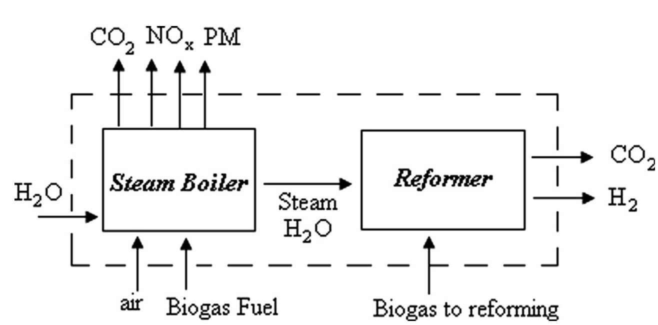

Fig. 7. Systems of the reformer and the steam boiler.

Table 4
Stoichiometric reactions for the biogas reform.

Steam reform (reactor 1)	$0.669CH_4+0.669H_2O \rightarrow 0.669CO+1.983H_2$
Dry reform (reactor 1)	$0.331CH_4+0.331CO_2 \rightarrow 0.662CO+0.662H_2$
Shift reform (reactor 2)	$1.331CO+1.331H_2O \rightarrow 1.331CO_2+1.331H_2$
Global steam reform (reactor 1+reactor 2)	$CH_4+2H_2O \rightarrow CO_2+4H_2O$

4.1. Hydrogen production cost

The hydrogen production cost involves the investment cost (boiler, reformer and accessories), as well as the operation and maintenance costs. Eq. (12) was used to calculate the price of produced hydrogen:

$$C_{H_2} = \frac{Inv_{REF}{}^{*}f}{H.E_{H_2}} + C_{OP} + C_{MAN} \tag{12}$$

The available power contained in the hydrogen generated from the reformer is calculated as follows:

$$E_{H_2} = \dot{m}_{H_2} \times LHV_{H_2} \tag{13}$$

4.2. Operational cost

The operational cost depends on the heat source and the used fuel in the reforming process. In the studied case, the biogas was considered as a fuel. The operational cost is obtained by the following equations.

$$C_{OP} = \frac{E_{FUEL}{}^{*}C_{FUEL}}{E_{H_2}} + \frac{E_{BIOGAS}{}^{*}C_{BIOGAS}}{E_{H_2}} \tag{14}$$

$$E_{BIOGAS} = \dot{m}_{BIOGAS} \times LHV_{BIOGAS} \tag{15}$$

$$E_{FUEL} = \dot{m}_{FUEL} \times LHV_{FUEL} \tag{16}$$

According to Kothari et al. [21], the maintenance cost of the reforming system can be considered as 3% of the investment cost, as shown in the following equation.

$$C_{MAN} = 0.03.\frac{Inv_{REF}{}^{*}f}{H.E_{H2}} \tag{17}$$

4.3. Annuity factor

The annuity factor is calculated by the following equaions.

$$f = \frac{q^k * (q-1)}{q^k - 1} \tag{18}$$

$$q = 1 + \frac{r}{100} \tag{19}$$

The following considerations were assumed in this study:

– The investment cost in a reformer system was considered as being US$ 15,000 (according to the experimental data).
– Annual interest rate of 20% [22].
– Equivalent period of operation: H=5,110 h/year, 5,840 h/year and 6,570 h/year, considering 12 h, 14 h, and 16 h a day respectively and 365 days per year.
– The low heating value (LHV) of hydrogen: 119,742.48 kJ/kg [18], methane: 49,934.28 kJ/kg [19] and for biogas: 37,850 kJ/kg [23].
– According to Tolmasquim [23], the biogas generation cost considered was US$ 0.0518/kWh.
– The boiler efficiency was estimated as 80% [19] and the energy consumed by the reformer system was calculated using the following equation.

$$E_{FUEL} * \eta_{Boiler} = E_{STEAM} \tag{20}$$

Considering a biogas reformer efficiency of 80% and the mentioned boiler efficiency, the necessary biogas flow in the boiler to produce 1 Nm^3 of hydrogen is 0.008 kg/h, and the biogas flow in the reformer is 0.34 kg/h. Then, the production cost of 1 Nm^3/h of hydrogen by biogas reforming is shown in Fig. 8.

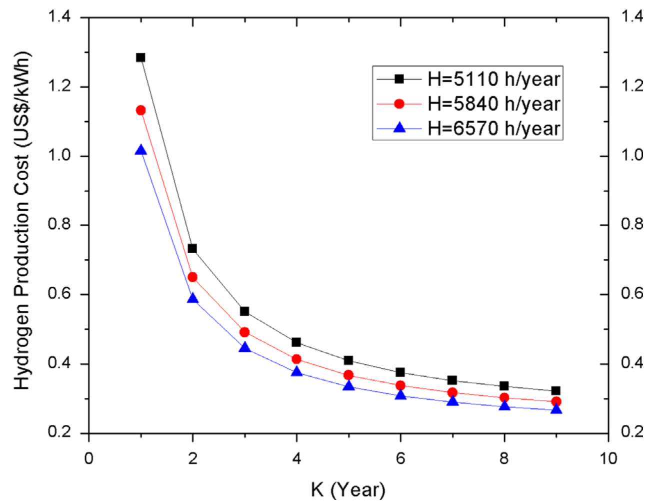

Fig. 8. Hydrogen production cost as a function of payback period.

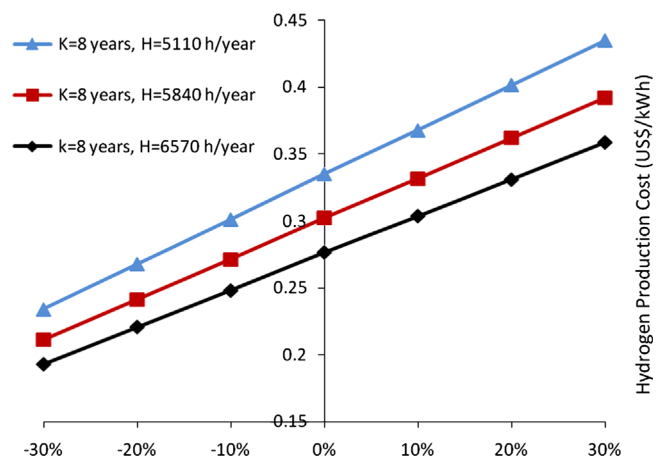

Fig. 9. Hydrogen production cost varying the main studied variables.

It is possible to observe in Fig. 8 that, from 8 years onwards, the hydrogen production cost tends to be constant, meaning that the investment cost in the reform process was amortized. The better hydrogen production cost is for an operation period of 6570 h/year, showing that the higher operation period leads to reduce the hydrogen production cost.

4.4. Sensitivity analysis

The economic model analysis of a project requires the use of data considered as certain and constant however, this rarely occurs, because these data are estimated and they show a picture of the reality. In the case studied the main variables studied are the investment, operation and maintenance and each of these variables could be modified over the time. Therefore, it is essential to apply a method that allows determining the influence of the variables change on the expected results of the process. Through the sensitivity analysis the intensity in which the main variables affect the final results of the projectis verified. Fig. 9 shows the sensitivity analysis of the principal variables in the hydrogen production cost through the biogas reforming process.

The analysis was performed for a variation range of ±30% from the values in the basic scenario of the principal variables for a payback period of 8 years.

The 8 years, set for the basic scenario was chosen due to the fact that it is from this period the hydrogen production cost tends to be constant. In this context, as shown in Fig. 9, the hydrogen production cost ranges from 0.2 to 0.35 US$/kWh for 6570 h/year, from 0.21 to 0.50 US$/kWh for 5840 h/year and 0.24 to 0.43 US $/kWh for 5110 h/year. These values show that, in fact, the variables affect the final results of the project to have a margin of variation in the hydrogen production cost.

5. Ecological analysis

The ecological analysis was performed to evaluate how pollutant is a biogas reforming system. This analysis was based on concepts of equivalent carbon dioxide, pollutant indicator, and ecological efficiency.

5.1. Equivalent carbon dioxide

The equivalent carbon dioxide $(CO_2)_e$ is composed of an hypothetical pollutant concentration factor that is shown in Eq. (21). For the calculation of this coefficient, the maximum value for the CO_2 concentration is divided by the corresponding air quality standard for CO, CH_4, NOx, SO_2 and PM [24].

$$(CO_2)_e = CO_2 + 21CH_4 + 80SO_2 + 50NO_x + 67PM \tag{21}$$

5.2. Pollutant indicator

The best fuel from the ecological standpoint is the one which produces lower emission of $(CO_2)_e$ when used to generate energy. In order to quantify this environmental impact, the pollutant indicator (Π_g) is defined by the following equation [25].

$$\pi_g = \frac{(CO_2)_e}{Q_i} \tag{22}$$

5.3. Ecological efficiency

The ecological efficiency is an indicator which allows the evaluation of the systems performance, according to pollutants emissions, by hypothetically comparing the integrated pollutants emissions $(CO_2)_e$ with the existing air quality standards. The conversion efficiency is also considered as a determining factor on the specific emissions, expressed by a fraction Eq. (23) which can be used for determining the ecological efficiency [24]:

$$\varepsilon = \left[\frac{0.204 \times \eta_{system} \times \ln(135 - \Pi_g)}{\eta_{system} + \Pi_g}\right]^{0.5} \tag{23}$$

where ε comprises, in a single coefficient, the aspects that define the environmental impact intensity and it is in the range between 0 and 100%. The situation that is considered infeasible from the ecological point of view when $\varepsilon = 0$; however, $\varepsilon = 100$ indicates an ideal situation from the same point of view [25].

5.4. Methodology and results

The theoretical study of the biogas steam reforming considered that all energy consumed by the process was generated from a boiler fed by biogas. It was also assumed that the biogas was burned after the purification process described by the following equation [26]:

$$0.754CH_4 + 0.243CO_2 + x(\beta O_2 + 3.7\beta N_2) \rightarrow CO_2 + 1.51H_2O + 3.7x\beta N_2 + x(\beta - 1)O_2 \tag{24}$$

where $\beta = 1,20$ (biogas burning in boiler with 20% of excess air) [27]

For the study of the environmental impact of this system, besides the emissions linked to the boiler, the emissions linked with steam reforming were calculated, and for that, the final stoichiometrical reaction of steam reforming was considered, as shown in the following equation.

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \tag{25}$$

The emissions of each process are shown in Table 5.

Table 5
Emissions during the biogas reform process.

Elements	Biogas combustion (kg/kg of biogas)	Steam reform (kg/kg of biogas)
$(CO_2)_e$	1.93	1.43

With these emission values, it was possible to calculate the equivalent carbon (CO_2)e, the pollutant indicator (Π_g) and, considering the overall efficiency of the reform process, it was possible to calculate the ecological efficiency (ε), as presented in Table 6

Table 6
Values of (CO_2)e, π_g and ε.

(CO_2)e $(kg_{pollutants}/kg_{fuel})$;	3.36
Π_g (MJ/kg_{fuel});	0.089
ε (%)	94.95

It can be noticed that the ecological efficiency is 94.95% which is a good value. This value could be higher if it is included in the calculus the negative environmental impact prevented, in the case that the biogas was released directly to the environment instead be reformed to produce hydrogen.

The major difference between the emissions, during the natural gas and biogas reforming process, is that the emissions of CO_2 from natural gas reforming contribute to global warming and the CO_2 from biogas reforming does not. It can be explained by the fact that CO_2 from biogas is from recently alive plant matter (even if it was fed to animals), it is part of a CO_2 cycle – i.e. CO_2 given off by burning biogas is absorbed by plants that will provide future biogas; besides that animal manures release methane into the atmosphere – about 10% of the methane emissions in the US come from animals, according to one survey [28]. Methane is a more potent greenhouse gas than CO_2, so it is a good idea to use it to produce hydrogen rather than releasing it.

6. Conclusions

According to the work developed, the steam reforming of biogas can be considered a feasible alternative for hydrogen production that decreases the negative environmental impact that causes the use of natural gas as a principal raw material for this purpose, but with similar levels of efficiency. Since the biogas has a composition similar to the natural gas, great changes in technology of steam reforming are not needed, since it is known that the natural gas is responsible for 50% of the world production of hydrogen.

The economical analysis showed that the hydrogen production cost decreases with the increase of the payback period and the equivalent period of operation, and can achieve 0.27US$/kWh with a payback period of 8 years.

The calculation of Carbon Dioxide Equivalent and the Pollutant Indicator for the biogas steam reforming using biogas as a source of heat allowed the determination of the ecological efficiency of this type of hydrogen production process. The results of these analyses showed that the process of producing hydrogen by biogas steam reforming is an environmentally promising technology due to the high value of ecological efficiency, 94.95%, even without considering the cycle of CO_2.

Finally, due to the fact that the biogas can be produced anywhere in large quantities and from different sources, and after an assessment of the hydrogen production by the biogas steam reforming process including the analysis of the technical aspects (reforming system, physicochemical analysis), economic aspects (cost of hydrogen production, US$/kWh) and ecological aspects involved in the process, it is possible to conclude that this is a technically and economically feasible technology for hydrogen production with a lower environmental impact than the production of this gas through the reforming of the natural gas. This study can contribute to the development of technologies fueled by hydrogen and could help decision makers to choose different routes for hydrogen production for the future projects.

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